

# APPARATUS AND PROCESS FOR PREPARING SORBENTS FOR MERCURY CONTROL AT THE POINT OF USE

## 5 CROSS REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Patent Application No. 60/460,478, filed April 3, 2003, the entire disclosure of which is hereby incorporated herein by reference.

## 10 FIELD OF THE INVENTION

The present invention is directed generally to treatment of gases to remove controlled materials and specifically to the treatment of flue gases to remove mercury and other contaminants.

## 15 BACKGROUND OF THE INVENTION

Each year, the emission of air toxics from combustion sources is being subjected to increasingly strict regulations. These regulations include not only existing regulations, such as the U.S. Clean Air Act as amended in 1970, 1977, and 1990, the National Energy Act, and the National Primary and Secondary Ambient Air Quality Standards, but also pending  
20 regulations that will require the removal of certain air toxics from utility plant flue gas. Title III of the Amendments governs air toxics. As used herein, an "air toxic" refers to the 189 chemicals listed in the Clean Air Act. Air toxics are present in the flue gas of combustion sources and appear both as particulate metals such as nickel, arsenic, and chromium in flyash particles and as vapor phase metals such as mercury, selenium, halogens, and halides and

organic vapors. Vapor phase air toxics are commonly present in flue gas in trace concentrations of parts per million or less and therefore can be difficult to remove to comply with pertinent regulations.

Several systems have been developed to remove trace quantities of air toxics from flue gas. The systems have had varying degrees of success.

In one system, activated carbons and carbons treated chemically to produce sulfide or iodide compounds with mercury are injected into a gas stream ahead of a particulate collection device, such as a Fabric Filter (FF), ElectroStatic Precipitator (ESP), Spray Dry Absorber (SDA), and Flue Gas Desulfurization (FGD) device. The activated carbon is typically introduced into the gas stream by blowing the carbon, in a dry particulate form, into the gas stream. While in flight, the carbon reacts with the entrained air toxics and binds the air toxics to the surfaces of the carbon. The air toxic-containing carbon is then removed by the FF, ESP, SDA, and/or FGD.

The carbons used for the mercury removal process are generally of high surface area and ground by the manufacturer to a small particle size, typically in the range of 10 microns to 100 millimeters. Manufacturers make different grades of carbon depending on the specific properties desired for a particular application. Activated carbon is manufactured in a finished form at centralized manufacturing locations. The material is then shipped in bulk form over long distances to end user locations using various means, such as supersacks, rail car and truck.

## SUMMARY OF THE INVENTION

These and other needs are addressed by the various embodiments and configurations of the present invention. The present invention is directed to the comminution of a sorbent before introduction into a contaminated gas stream. As used herein, a "sorbent" refers to a substance having a capacity to adsorb, absorb, and/or otherwise entrap a desired material, such as an air toxic.

In one embodiment, the present invention is directed to a method for treating a contaminated gas stream comprising one or more contaminants that includes the steps of:

(a) combusting a feed material, to produce a contaminated gas stream;

(b) comminuting a plurality of sorbent particles having a first size distribution to form comminuted sorbent particles having a second size distribution, the second size distribution being smaller than the first size distribution; and

(c) thereafter introducing the comminuted sorbent particles into the gas stream to remove the one or more contaminants.

The comminution of the sorbent particles is typically performed on site and without intermediate storage. As used herein, "on-site" refers to the general area of the combustion chamber, utility or other type of plant and can include transporting continuously the sorbent particles from a location near the chamber, utility or plant by means of a conveyor, slurry line, or pneumatic line, even though the location is not on the physical site of the chamber, utility or plant. The time between the completion of the comminuting and introducing steps is preferably no more than about 1 hour, no more than about 30 minutes, no more than about 10 minutes, no more than about 1 minute, preferably no more than about 30 seconds, and

most preferably no more than about 1 to 10 seconds. Normally, the comminution device is at least substantially co-located with the nozzles and remainder of the sorbent injection system.

While not wishing to be bound by any theory, it is believed that the sometimes low  
5 contaminant removal rates of sorbents in commercial applications are due in large part to the agglomeration of particles during transportation from the manufacturer to the end user and during on-site storage before use. Agglomeration can dramatically change the effective particle size distribution. In other words, agglomeration can cause a larger mean and median sorbent particle size. When the sorbent is introduced into the gas stream, the larger particle  
10 size distribution provides, per unit of sorbent, fewer particles in the gas stream for contaminant sorbtion and removal. This can cause a substantially reduced sorbent removal efficiency. To attempt to overcome this problem, end users can introduce more sorbent per unit volume of gas stream, thereby resulting in much higher operating costs.

The method can have a number of benefits compared to existing processes. First, on-  
15 site milling can provide a sorbent particle size distribution that is relatively small and highly effective in removing contaminants. As will be appreciated, a finer particle size provides a greater number of particles in the gas stream for a given amount of sorbent, a high mass transfer rate to the gas stream, and a smaller interparticle distance in the gas stream. These factors can provide a higher rate of contaminant removal. On-site milling can also expose  
20 fresh, unreacted (more active) surfaces for contaminant capture. As will be appreciated, certain sorbents can react with the surrounding atmosphere when exposed to the atmosphere for prolonged periods, such as during shipping, thereby reducing the air toxic capacity of the

sorbent. Second, the use of on-site milling permits the sorbent to be shipped as larger particles, thereby providing higher packing densities during shipment, greater ease of material handling, less product loss during transportation and handling, and lower transportation and operating costs. For example, raw (unmilled) activated carbon can be produced at centralized facilities, shipped to the end user site, and there processed (milled) to produce a desired particle size. As will be appreciated, the bulk density of the finished (milled) activated product is much less than the bulk density of raw activated carbon. Third, the sorbent processed on site can meet tighter specifications, particularly size distribution specifications. The on-site processed sorbent particles can, for example, have a narrower and smaller size distribution than milled sorbent particles shipped long distances. Fourth, on-site processing permits additional ingredients (such as other sorbents) to be introduced into the mill along with the sorbent to produce an enhanced sorbent material. The sorbent material, for instance, can be a customized blend having desired properties that is uniquely suited for the specific application.

These and other advantages will be apparent from the disclosure of the invention(s) contained herein.

The above-described embodiments and configurations are neither complete nor exhaustive. As will be appreciated, other embodiments of the invention are possible utilizing, alone or in combination, one or more of the features set forth above or described in detail below.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a block diagram of a flue gas processing system according to an embodiment of the present invention;

Fig. 2 is a diagram depicting a portion of the sorbent injection system according to an embodiment of the present invention;

Fig. 3 is a flow chart of the operation of the gas processing system of Fig. 1; and

Fig. 4 is a graph showing mercury control using sorbents of 6 micrometers mass mean particle diameter compared to sorbents of 18 micrometers mass mean particle diameter.

## DETAILED DESCRIPTION

A first embodiment of the flue gas processing system of the present invention is shown in Fig. 1. The system 100 includes a sorbent injection system 112, particle removal device 104, and further treatment device(s) 116, all positioned downstream of boiler 108. The treated gas 120 is discharged through a stack into the exterior environment. As will be appreciated, the boiler 108 combusts a suitable fuel, typically coal. The temperature of the flue gas 144 outputted from the boiler 108 typically at least about 1,000 degrees F. When a heat exchanger (not positioned) is positioned downstream of the boiler 108 and upstream of the injection system 112, the temperature of the flue gas 148 outputted by the heat exchanger is in the range of about 250 to about 650 degrees F (which is above the acid dew point).

The flue gas 144 includes a number of controlled contaminants. For example, a typical flue gas 144 includes from about 100 - 4,000 ppm sulfur oxides, from about 50 -

2,000 ppm nitrous oxides, and from about 1 - 200 ppm hydrogen chloride; from about 1 - 20 grains per actual cubic feet of particulates (at least most of which are flyash); and from about 0.1 ppb to about 10 ppm vapor phase air toxics. These amounts of these contaminants must be reduced to acceptable levels before emission of the flue gas into the environment.

5           The particulate removal device 104 is any suitable device for effecting removal of at least most of the rejected sorbent particles. Typically, the device is a fabric filtration device such as a baghouse, a (wet or dry) electrostatic precipitator, a scrubber, a flue gas desulfurizer, and/or a combination thereof. The device 104 typically removes at least about 95% and more typically at least about 99% of the entrained particles from the flue gas 144.

10           The further treatment device(s) 116 can remove contaminants not removed sufficiently by the sorbent. Typically, the device(s) include a flue gas desulfurizer and is preferably a wet flue gas desulfurizer. The flue gas desulfurizer 116 typically removes at least most of the acid gases (*e.g.*, sulfur dioxide and hydrogen chloride) and some of the air toxics. Examples of desulfurizers include spray towers, limestone, magnesium limestone,  
15 ammonia, forced oxidation, bubbling bed reactors, wet scrubbers, semi-wet scrubbers, dry scrubbers, and combinations thereof. The preferred desulfurizer is a wet scrubber having a vertical tower construction. The specific scrubbing agent(s) in the absorption zone depend on the contaminants being removed. Examples of scrubbing agents include an alkaline solution, such as a calcium-based slurry (such as a solution containing lime) and a sodium-  
20 based solution, for removing sulfur oxides (*i.e.*, SO<sub>x</sub>, where x is 2, 3, or 4) and an ammonia-based solution, metals such as iodine dissolved in an organic solvent, organic solvents such as methanol, and a solution of Fe(II) ions and thiosulfate in a miscible mixture of water and

alcohol or a non-aqueous solvent, an emulsion of water-in-organic sulfoxides for removing both sulfur oxides and/or nitrous oxides (*i.e.*, NO<sub>x</sub>, where x is 1, 2, or 3). Typically, the flue gas desulfurizer 116 removes at least about 90% and more typically at least about 98% of the SO<sub>2</sub>; and at least about 80% and more typically at least about 90% of the HCl present in the flue gas. The desulfurizer 116 typically reduces the temperature of the flue gas to the bulk water dew point, which is commonly about 52.5°C.

As will be appreciated, a flyash particle removal system and flue gas desulfurizer can be positioned upstream of the sorbent injection system 112 as described in copending U.S. Patent Application Serial No. \_\_\_/\_\_\_,\_\_\_, filed \_\_\_\_\_, 2004, entitled "METHOD FOR REMOVING AIRBORNE TOXIC MATERIALS FROM FLUE GAS" to Durham, et al., which is incorporated herein by this reference. The flyash particles may be removed before injection of the sorbent particles by the sorbent injection system 112 or simultaneously with the removal of the sorbent particles by the particle removal system 104.

When the FGD device precedes or is upstream of the injection system 112, the sorbent may be selected to remove contaminants in addition to air toxics. The desulfurized flue gas output by the FGD commonly includes from about 5 to about 200 ppm sulfur oxides, and from about 0.2 to about 40 ppm hydrogen chloride. In the desulfurizer, it is common to have some acid gas, such as sulfur trioxide and sulfuric acid, form an acid mist that must be removed to produce a compliant waste gas. The acid mist forms when sulfur-containing gases are exposed in the desulfurizer with a scrubbing agent that is an alkaline medium to remove a majority of the sulfur species. A portion of the sulfur species forms the acid mist that is typically not captured by the desulfurizer.



The sorbent injection system 112 further treats the gas to produce a compliant waste gas. The sorbent injection system 124 can have a number of differing configurations depending on the sorbent employed. The sorbent may be configured to remove air toxics, sulfur oxides, nitrous oxides, hydrochloric acid vapor, hydrogen sulfide vapor, acid gas, hydrogen fluoride, and/or condensibles (which include organic compounds). The sorbent preferably is a free flowing particulate (carbon or non-carbon based) solid, such as activated carbon, molecular sieves, zeolites, chars, soots, aluminas, magnesium oxide, limestones, silicates such as the sorbents manufactured by Amended Silicates, LLC, mineral sorbents such as the sorbents manufactured by CDEM Holland B.Z., or another suitable sorbent material and/or carbon, molecular sieves, zeolites, and other impregnable substrates including on exposed surfaces various substances, such as metals, metal compounds, sulfur, sulfur compounds, and combinations and mixtures thereof.

Examples of suitable sorbents are discussed in U.S. 6,558,642; 6,533,842; 6,524,371; 6,375,909; 6,372,187; 6,322,613; 6,270,679; 6,136,281; 6,103,205; 5,900,042; 5,695,726; 5,670,122; 5,607,496; 5,569,436; 5,460,643; 5,409,522; 5,322,128; 5,248,488; 5,245,106; 5,225,175; 5,141,724; 5,120,515; 5,085,844; 5,064,626; 4,933,158; 4,902,662; 4,892,567; 4,877,515; 4,843,102; 4,834,953; 4,814,152; 4,786,484; 4,786,483; 4,771,030; 4,764,219; 4,721,582; 4,709,118; 4,500,327; 4,474,896; 4,459,370; 4,369,167; 4,196,173; 4,101,631; 4,094,777; and 3,755,161, each of which is incorporated herein by this reference.

A preferred air toxic absorbent is activated carbon. Activated carbon is a mature and widely used technique for removing air toxics, such as mercury, from gas streams. Activated carbon is finely divided which allows it to be introduced into a flowing gas stream and flow

along with the gas stream. Activated carbon, when entrained in the gas stream, has been proven to collect air toxics through in-flight capture.

As shown in Fig. 2, the injection system 124 typically includes a hopper 200 in fluid communication with a comminution device 204 that comminutes the sorbent 208 to a desired size range. The bulk sorbent 208 is typically delivered by a supersack, pneumatic rail car or pneumatic truck. The comminuted sorbent 300 is conveyed pneumatically via an air eductor (not shown) powered by an air line 216 supplying air from the air source 218 (or air compressor). As air passes through the air line 216 and past the eductor, solid particles outputted by the comminution device 204 are aspirated and conveyed (by dilute phase techniques) via air line 220 directly to a plurality of injection nozzles 224a-f and distributed substantially uniformly throughout the duct 228 as a plurality of solid particles.

The injection nozzles 224 can be in any suitable configuration, such as in a horizontal and/or vertical arrangement. Each nozzle typically includes a pipe header of approximately 2 to 6 inches in diameter having a plurality of about 1/4 to 1 inch nozzles for uniform particulate injection into the duct. The introduction rate of the sorbent is adjusted so that the gas downstream of the nozzles and upstream of the particle removal system 104 includes from about 0.5 to 20 pounds of sorbent per million actual cubic feet of gas. A preferred introduction rate is from about 3 to about 5 pounds of sorbent per million actual cubic feet of gas.

The size distribution of the comminuted sorbent 300 depends on the application. On the one hand, an extremely fine particle size distribution is desired to provide more particles for introduction into the gas stream, thereby providing a greater degree of contaminant

removal for a given amount of sorbent. On the other hand, if the particle size distribution is too fine the sorbent particle collection efficiency of the particle removal system 104 will decrease, potentially causing an unsightly plume when the gas 120 is discharged from the stack. The comminuted sorbent particles preferably have a  $P_{90}$  size ranging from about 0.5 to about 25 microns, more preferably from about 1 to about 10 microns, and even more preferably from about 0.2 to about 5 microns. Typically, no more than about 20% of the particles have a size greater than about 100 microns and even more typically a size greater than about 10 microns. Immediately before being inputted into the comminution device 204, the sorbent particles preferably have a  $P_{90}$  size ranging from about 10 microns to about 1 millimeter and no more than about 20% of the particles have a size greater than about 2 millimeters. The pre-comminuted sorbent can be in pelletized, granular, or powdered form.

To realize these fine particle sizes, and not intending to be limited by the particular device, the preferred comminution devices are a jet mill or agitated media attrition mill. As will be appreciated, a jet mill uses a high pressure fluid stream, such as air, an inert gas such as hydrogen, or a liquid such as water, to effect particle comminution or size reduction. The high pressure fluid is supplied to a grinding chamber via nozzles. High velocity (*e.g.*, sonic or supersonic velocity) fluid (liquid or gas) exiting the nozzles accelerates the particles introduced into the jet mill resulting in size reduction due to particle-to-particle collisions. The expanding fluid conveys the material to a particle size separator, such as a classifier, venturi, centrifuge, and the like, that rejects oversize material back to the grinding zone and allows a predetermined particle size to pass through. The particle size distribution can be adjusted by changing the setting(s) of the particle size separator, the air/liquid pressure, fluid

flow, or nozzle size and configuration. The particles can be introduced into the jet mill by any suitable technique, such as in a fluidized bed and entrainment in the high pressure gas stream itself. Any type of jet mill may be employed such as the pancake jet mill, the loop jet mill, the opposing-nozzle jet mill, the Majac mill, the Gem-T mill, the flooded grinding chamber mill, and the aeroplex or fluidized bed jet mill. Examples of suitable jet mills include the JET-O-MIZER™, ROTO-SIZER™, and ROTO-JET™ by Fluid Energy Processing and Equipment Company, the NETZSCH-CONDUX™ jet mill by Netzsch, the Attritor DIRECT OPPOSED JET MILL™, the Kurimoto CROSS JET MILL™, ALPINE 50 AS™ and 100AFG™ spiral jet mill, QYF™ fluidized-bed pneumatic jet mill, QYN™ ultrasonic pneumatic jet mill, SINGLE TRACK™ jet mill, SK JET-O-MILL™ CO-JET™ system, and the A-O™ jet mill. Examples of the agitated media attrition mills include, for example, Eirich Machines MAXXMILL™, and the Union Process Inc. ATTRITOR™. As will be appreciated, sensors, such as temperature, pressure and/or sound sensors, may be located within the mill and at the discharge of the mill to measure different processing parameters to measure the size of the sorbent particles created. The information received from the sensors can be used to control the mill operation to produce the desired particle size. The use of such sensors is further discussed in U.S. 6,318,649, which is incorporated herein by this reference.

For optimal results and to avoid reagglomeration, the comminuted sorbent particles are not commonly stored after comminution but introduced directly into the gas stream. Typically, the time interval between output from the comminution device to introduction into the gas stream is no more than about 1 hour, no more than about 30 minutes, no more than

about 10 minutes, no more than about 1 minute, preferably no more than about 30 seconds, and most preferably no more than about 1 to 10 seconds.

The operation of the system 100 will now be discussed with reference to Fig. 3.

5 In step 304, the sorbent particles are shipped, such as by pneumatic railcar or truck, to the end user from the manufacturer and stored in the hopper 200 by means of air line 230.

In step 308, the stored sorbent particles are transported via a device 212 to the comminution device 204. The device 212 can be any suitable feeding device, such as a rotary screw-type feeder, a conduit using gravity to induce sorbent displacement, pneumatic feed line using pressurized air and an eductor, and the like.

10 In step 312, the comminution device 204 effects size reduction of the sorbent particles, such as by high velocity gas flow, to realize the desired size range. The size reduction is typically caused by high velocity particle-to-particle contact and/or particle-to-stationary surface contact. The typical size reduction factor of the sorbent particles in this step is at least about 5 and more typically ranges from about 10 to about 200.

15 In step 316, the comminuted sorbent 300 is aspirated continuously into a pressurized gas injection stream and transported by the air line 220 to the injection nozzles spaced at intervals throughout the cross section of the contaminated gas stream. As noted, it is preferred that the outputted comminuted sorbent 300 be fed continuously to the air line 220 without intermediate storage to avoid particle reagglomeration.

20 In step 320, the nozzles inject the comminuted sorbent particles 300 substantially uniformly throughout the gas stream. The contaminants are captured by the sorbent particles

while the particles are in flight and by the sorbent particles that are captured in the particle removal device.

Entrained air toxics and other contaminants are captured effectively by the entrained sorbent particles. Typically, at least about 50%, and more typically at least about 75% of the desired contaminants, typically air toxics, are captured by the sorbent particles. As an example of collecting mercury (an air toxic), mercury in the gas leaving the boiler at a concentration of 1-20  $\mu\text{g}/\text{m}^3$  can be collected at an efficiency of from 10 - 99% depending on the amount and capacity of the sorbent being injected by the injection system. In this case the output waste gas to the stack comprises no more than about 0.01 - 18  $\mu\text{g}/\text{m}^3$  of mercury and typically no more than about 0.05 - 10  $\mu\text{g}/\text{m}^3$  of mercury.

In step 324, the contaminant-laden particles are collected by the particle removal system and removed from the gas stream. The collected sorbent particles are removed periodically or continuously from the collection surface of the particle removal system by any suitable technique, such as liquid transfer, rapping, reverse airflow and the like.

## EXPERIMENTAL

### Example 1

The following Example describes improved mercury control in flue gas achieved with finely ground sorbent particles.

This Example was carried out on the flue gas from an operating coal-fired power plant. A number of carbon sorbents, including DARCO FGD manufactured by Norit Americas (Marshall, TX) with a mass mean particle diameter of approximately 18 micrometers, was compared to DARCO INSUL, also manufactured by Norit Americas, with

a mass mean particle diameter of approximately 6 micrometers, was injected into the flue gas, downstream of (i.e., after) an electrostatic precipitator (ESP), and upstream of a baghouse (fabric filter.) Flue gas temperature was approximately 300 degrees F. Mercury concentration was measured by a Semi-Continuous Emissions Monitor (S-CEM), in the following locations: upstream of the ESP and downstream of both the sorbent injection site and the baghouse.

Figure 4 shows the results. The X-axis depicts the amount of carbon injected into the flue gas per unit volume of flue gas (lbs carbon per million actual cubic feet of flue gas treated, lbs/MMacf). The Y axis shows the measured mercury removal rate, measured as a percentage removed between the upstream sampling location and downstream sampling location. The percentage removal was measured for each type of sorbent. Mercury removal results were obtained for one injection concentration of DARCO INSUL only. The results indicated that DARCO INSUL, the 6 micrometer mass mean particle diameter sorbent, was more effective than the 18 micrometer mass mean particle diameter sorbent to remove mercury from flue gas streams.

A number of variations and modifications of the invention can be used. It would be possible to provide for some features of the invention without providing others.

The present invention, in various embodiments, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various embodiments, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the present invention after understanding the present disclosure. The present invention, in various embodiments, includes providing devices and

processes in the absence of items not depicted and/or described herein or in various embodiments hereof, including in the absence of such items as may have been used in previous devices or processes, e.g. for improving performance, achieving ease and/or reducing cost of implementation.

5           The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the invention are grouped together in one or more embodiments for the purpose of streamlining the disclosure. This method of disclosure is not to be interpreted as reflecting  
10           an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the invention.

15           Moreover though the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, e.g. as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including  
20           alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures,



functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.